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The Crystal Structure of Methyl β-Maltopyranoside

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The crystal structure of methyl β-maltoside monohydrate was solved by the convolution of the Patterson projection with E maps obtained by a sign-correlation procedure on the $h0l$ reflections. The structure was refined three-dimensionally by anisotropic least squares to give a final R value of 0·056 for 1375 reflections. The space group is $C2$, with $Z=4$ and unit-cell dimensions $a=22{\cdot}664$, $b=4{\cdot}841$, $c=17{\cdot}316$ Å, $\beta=117{\cdot}27°$. All the hydrogen atoms were located on difference syntheses, but were not refined. The α 1–4 linked glucopyranose residues have the $C1$ chair conformation with interatomic distances which are normal for single bonds, with the exception of the C–O bonds. The methyl β-glycosidic bond, C(1′)–O(1′)CH_3, is 1·375 Å. It is significantly shorter than the mean value of 1·427 Å, in contrast to the α-glycosidic link joining the two glucopyranoside residues, which is 1·416 Å. This difference in the glucosidic bond lengths appears to be correlated with the relative lengths of the C–O ring bonds, which are observed equal in one ring (C′–O′) and unequal in the other (C–O). All the oxygen atoms, except the ring and bridge oxygen atoms, are associated with a hydrogen bonding scheme, which includes one intramolecular bond and consists of closed rings and helical chains.

Introduction

Maltose is an important disaccharide, of considerable interest as a model compound for the structure of amylose and starch. Hybl, Rundle & Williams (1965) have determined the crystal structure of the cyclohexaamylose–potassium acetate complex which contains the equivalent of three maltose units. It is the purpose of this investigation to determine the detailed conformation of the maltose molecule and provide more precise data on interatomic distances and the hydrogen bonding in the solid state.

Maltose was shown by Haworth, Long & Plant (1927) to consist of two D-glucopyranose residues connected between carbon atoms 1 and 4 by an α-glucosidic link, thereby differing from cellobiose, which has a similar structure with a β 1–4 linkage. Bentley (1959) concluded from chemical evidence that in cellobiose both glucose units have the chair-shaped $C1$ conformation and this has been confirmed by the crystal structure determination (Jacobson, Wunderlich & Lipscomb, 1961; Brown, 1966). Bentley's results on maltose were less definitive, since he assumed that both glycosidic bonds were equatorial and interpreted the observed complexing reactions with cuprammonium solution to require a 'skew' intermediate for the nonreducing glucose unit. We have examined the methyl glucoside derivative rather than maltose itself because these results referred more directly to that compound.

Crystal data

Methyl β-maltoside monohydrate crystals were obtained through the courtesy of Dr Bentley (Bentley, 1959) of the Graduate School of Public Health, University of Pittsburgh. They were in the form of thin, transparent needles elongated along the b axis. The cell parameters were measured with Cu $K\alpha_1$ and Cu $K\alpha_2$ radiation on a Picker 4-angle automatic diffractometer. The crystal density was determined by flotation in a liquid mixture of carbon tetrachloride and carbon disulfide.

Methyl β-maltoside monohydrate, $C_{13}O_{11}H_{24}.H_2O$, M.W. 374·35.

Monoclinic, space group $C2$ from the systematic extinctions: hkl absent for $h+k=2n+1$.

$a=22{\cdot}644$ ($\sigma=0{\cdot}009$) Å
$b=\ 4{\cdot}841$ ($\sigma=0{\cdot}003$)
$c=17{\cdot}316$ ($\sigma=0{\cdot}007$)
$\beta=117{\cdot}27$ ($\sigma=0{\cdot}05$)°
$Z=4$
$D_m=1{\cdot}469$ ($\sigma=0{\cdot}004$) g.cm^{-3}
$D_x=1{\cdot}472$ g.cm^{-3}
$\mu_{\text{Cu }K\alpha}=11{\cdot}54$ cm^{-1}.

Experimental

The integrated intensity data were recorded initially on multiple-film equi-inclination Weissenberg photographs with Cu $K\alpha$ radiation. Of the 2169 theoretically possible reflections, 1256 were observed above the background of the film, and their intensities were estimated visually by comparison with a standard scale. No absorption corrections were made. The intensities were correlated and reduced to the structure amplitudes using an IBM 7090 program (Shiono, 1966*a*) which was based on the procedure by Hamilton, Rollett & Sparks (1965).

After the structure was solved, another set of data was collected on a Picker 4-angle automatic diffractometer from a crystal with approximate dimensions of 0·02 × 1·00 × 0·15 mm. A $\theta/2\theta$ scanning mode over 2° was used to measure 1602 independent reflections with 2θ values below 130°, of which 1375 reflections had intensities significantly above the background. Stationary background measurements were made at both ends of the 2° scan range of each reflection. The same number of equivalent reflections were measured in two different quadrants of the reciprocal lattice. However, the reference reflections which were repeated in intervals of approximately every 100 reflections were found to be significantly more constant for one set and these data were used in the refinement rather than the mean values. No absorption corrections were applied in reducing to structure amplitudes.

Determination of the structure

The structure was solved from the 307 observed $h0l$ reflections. The structure factors were converted to the normalized $|E_{hkl}|$'s (Hauptman & Karle, 1953), two linearly independent reflections were arbitrarily given positive signs in order to fix the origin and twelve more reflections with large $|E|$ values were given symbolic signs. The Beurskens (1963) IBM 1620 program was then used to determine the most probable values of the symbols by first applying the Sayre (1952) equation to obtain sign relationships and then eliminating unknowns by a sign correlation procedure. Since the centrosymmetric projection of a monoclinic space group lacks the symmetry relations which generate negative signs, the trivial set of all positive signs has the highest probability. The four symbols of lowest probability were therefore given all combinations of plus and minus signs, except all positive, leaving 15 possible solutions of 90 to 120 signs each. Of the fifteen alternative two-dimensional E maps (Karle, Hauptman, Karle & Wing, 1958) five showed some features of the molecule, but it was impossible to select the correct one. A two-dimensional (E^2-1) Patterson synthesis indicated the orientation of the pyranose rings but could not be interpreted in detail. Each of the five most probable trial E maps was therefore convoluted with the Patterson function by finite integration, using an IBM 1620 program prepared by Corfield (1965). This led to a recognition of the structure in one of the possible solutions. The first structure factor calculation for thirteen carbons and twelve oxygens gave an R value of 0·52 for all observed reflections. Successive Fourier syntheses, difference Fourier syntheses, and some trial and error calculations led to an isotropic least-squares refinement which gave an R value of 0·18 for the $h0l$ data. By fixing one particular atom, the y coordinates were then easily determined using an assumed configuration of the molecule consistent with the resolved projection. Two cycles of isotropic least-squares refinement with the three-dimensional data gave an R value of 0·19.

Refinement of the structure

The refinement of the positional parameters, the anisotropic thermal parameters for the carbon and oxygen atoms, and one scale factor was carried out by the full-matrix least-squares IBM 7090 program on the intensity data collected by Picker diffractometer. The full-matrix least-squares program used was written by Busing, Martin & Levy (1962) for an IBM 7090 computer and modified by Shiono (1966*b*). Hughes's (1941) weighting scheme was used initially but Cruickshank's (1961) weighting scheme was substituted in the final stage in order to make $[\Sigma w(F_{\text{obs}}-F_{\text{cal}})^2/(\text{no. of reflections}-\text{no. of parameters})]^{\frac{1}{2}}$ approximately equal to unity. Because of the limited number of parameters that could be simultaneously varied by the program, each cycle of refinement was carried out in two stages by fixing the thermal parameters of eight neighboring atoms in each stage. Two cycles of anisotropic least-squares refinement reduced R to 0·077. All the hydrogen atoms except one on the methyl group, which is located near the direction of the large thermal motion of the carbon atom, were clearly revealed in two successive difference Fourier syntheses, with reasonable bond lengths and bond angles with respect to the carbon and oxygen atoms. Two more cycles of least-squares refinement, including all the hydrogen atoms, gave the final R value of 0·056. The positional parameters of the hydrogen atoms were not refined and they were assigned the same thermal parameters as those of the carbon or oxygen atoms to which they are bonded. The final positional and thermal parameters are listed in Table 1, and the corresponding structure factors are given in Table 2. The principal axes of the thermal ellipsoids are given in Table 3.

Description of the structure

The systematic name for methyl β-maltoside monohydrate is methyl 4-*O*-α-D-glucopyranosyl-β-D-glucopyranoside monohydrate (or methyl *O*-α-D-glucopyranosyl-(1→4)-β-D-glucopyranoside monohydrate). The identification of the atoms used in this paper is shown in Fig. 1.

Both pyranose rings have the chair $C1$ form and there is no evidence of any departure from this strainless conformation towards a skew form such as suggested by Bentley (1959). The conformation angles of the rings are given in Table 4. They are in the same range as those observed in other pyranose sugars (*cf.* Kim & Jeffrey, 1967). The conformation about the α 1–4 linkage is such that the midplanes O(1′)C(1′)C(4′), O(4)C(4)O(1) through the glucose units make angles of 171 and 165° respectively with the plane of the C(4′)O(1)C(1) link. This small twist in the 'backbone' of the molecule is such as to bring the intramolecular hydrogen-bonded O(2) and O(3′) closer and leave more space between the primary alcohol groups for the hydrogen-bonded water on the other side of the molecule. It is worth remarking that the maltose 'backbone' in this structure is straighter than that observed in cellobiose (Brown, 1966), where the comparable angles are 165 and 138°, again with the twist so as to shorten the intramolecular hydrogen-bond distance on one side of the molecule. The conformation angles of the primary alcohol groups are such that C(6)–O(6) has the '+sc' (+syn-clinal) (Klyne & Prelog, 1960) orientation, as was found in all the glucose residues in both cyclohexaamylose–potassium iodide (Hybl *et al.*, 1965) and cellobiose (Brown, 1966). The C(6′)–O(6′) bond has the '−sc' (−syn-clinal) orientation, as was found in sucrose (Brown & Levy, 1963).

Within one molecular unit of methyl β-maltoside monohydrate, there are three hydrogen bonds. One is formed between O(2) and O(3′) on one side of the molecule, and the other two link the water molecule with the two primary alcohol groups, O(6)H and

Table 1. *Fractional atomic coordinates and thermal parameters**

The estimated standard deviations are given in parentheses and refer to the last decimal positions of respective values. The expression for the temperature factor exponent consistent with the β values is:

$$-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl).$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	0·3740 (2)	0·0000	0·1920 (2)	0·0016 (1)	0·0235 (16)	0·0027 (1)	−0·0009 (3)	0·0012 (1)	−0·0012 (4)
O(2)	0·3363 (2)	0·2878 (13)	0·0376 (2)	0·0016 (1)	0·0393 (21)	0·0028 (1)	0·0020 (4)	0·0008 (1)	0·0036 (5)
O(3)	0·4224 (2)	−0·0017 (14)	−0·0160 (2)	0·0021 (1)	0·0551 (26)	0·0023 (1)	0·0042 (5)	0·0010 (1)	0·0013 (6)
O(4)	0·5314 (2)	−0·2924 (12)	0·1146 (2)	0·0018 (1)	0·0353 (22)	0·0034 (2)	0·0021 (4)	0·0014 (1)	0·0010 (5)
O(5)	0·4825 (2)	0·1633 (12)	0·2452 (2)	0·0013 (1)	0·0277 (16)	0·0026 (1)	−0·0009 (3)	0·0007 (1)	−0·0023 (4)
O(6)	0·5893 (2)	−0·1118 (12)	0·3797 (2)	0·0020 (1)	0·0340 (20)	0·0025 (1)	−0·0001 (4)	0·0007 (1)	0·0010 (5)
C(1)	0·4152 (2)	0·2130 (14)	0·1877 (3)	0·0015 (1)	0·0214 (22)	0·0031 (2)	0·0000 (4)	0·0011 (1)	0·0004 (6)
C(2)	0·4044 (2)	0·2303 (14)	0·0948 (3)	0·0017 (1)	0·0240 (24)	0·0028 (2)	0·0008 (4)	0·0011 (1)	−0·0003 (6)
C(3)	0·4287 (2)	−0·0292 (14)	0·0693 (3)	0·0019 (1)	0·0213 (22)	0·0028 (2)	0·0004 (4)	0·0013 (1)	−0·0006 (6)
C(4)	0·5024 (2)	−0·0550 (14)	0·1336 (3)	0·0017 (1)	0·0247 (24)	0·0030 (2)	−0·0004 (4)	0·0010 (1)	0·0001 (6)
C(5)	0·5099 (2)	−0·0801 (15)	0·2259 (3)	0·0014 (1)	0·0298 (23)	0·0030 (2)	−0·0004 (5)	0·0010 (1)	0·0016 (6)
C(6)	0·5827 (2)	−0·0927 (17)	0·2938 (3)	0·0014 (1)	0·0430 (29)	0·0031 (2)	0·0006 (6)	0·0008 (1)	0·0018 (8)
O(1′)	0·2065 (2)	−0·0591 (15)	0·3382 (2)	0·0020 (1)	0·0653 (31)	0·0037 (2)	−0·0013 (5)	0·0017 (1)	−0·0021 (7)
O(2′)	0·1538 (2)	−0·1223 (14)	0·1537 (2)	0·0013 (1)	0·0569 (28)	0·0032 (2)	−0·0018 (4)	0·0006 (1)	−0·0025 (6)
O(3′)	0·2403 (2)	0·1351 (13)	0·0910 (2)	0·0016 (1)	0·0453 (24)	0·0022 (1)	−0·0013 (4)	0·0003 (1)	0·0008 (5)
O(5′)	0·3095 (2)	−0·0063 (12)	0·3511 (2)	0·0015 (1)	0·0395 (20)	0·0023 (1)	−0·0005 (4)	0·0008 (1)	−0·0005 (5)
O(6′)	0·4302 (2)	0·3018 (12)	0·3949 (2)	0·0017 (1)	0·0307 (19)	0·0032 (2)	0·0000 (4)	0·0005 (1)	−0·0004 (5)
C(1′)	0·2455 (2)	−0·1211 (16)	0·2986 (3)	0·0015 (1)	0·0366 (26)	0·0028 (2)	−0·0011 (5)	0·0011 (1)	−0·0018 (7)
C(2′)	0·2148 (2)	0·0079 (15)	0·2092 (3)	0·0013 (1)	0·0345 (25)	0·0031 (2)	−0·0001 (5)	0·0008 (1)	−0·0014 (7)
C(3′)	0·2617 (2)	−0·0275 (15)	0·1681 (3)	0·0011 (1)	0·0357 (25)	0·0022 (2)	−0·0012 (5)	0·0005 (1)	0·0001 (6)
C(4′)	0·3313 (3)	0·0653 (14)	0·2304 (3)	0·0012 (1)	0·0303 (24)	0·0026 (2)	−0·0003 (4)	0·0009 (1)	−0·0013 (6)
C(5′)	0·3550 (2)	−0·0730 (15)	0·3179 (3)	0·0014 (1)	0·0273 (23)	0·0030 (2)	0·0012 (5)	0·0011 (1)	0·0001 (6)
C(6′)	0·4241 (3)	0·0067 (16)	0·3852 (3)	0·0020 (1)	0·0356 (28)	0·0022 (2)	0·0010 (6)	0·0009 (1)	0·0005 (7)
C(7′)	0·2257 (3)	−0·2038 (27)	0·4178 (4)	0·0029 (2)	0·1091 (74)	0·0034 (3)	−0·0040 (11)	0·0018 (2)	−0·0002 (13)
O(W)	0·5643 (2)	0·3990 (14)	0·4424 (2)	0·0023 (1)	0·0454 (25)	0·0030 (2)	−0·0020 (5)	0·0009 (1)	0·0003 (6)

	x	y	z
H(O2)†	0·311	0·135	0·064
H(O3)	0·387	0·125	−0·060
H(O4)	0·542	−0·275	0·071
H(O6)	0·568	0·055	0·379
H(C1)	0·409	0·375	0·220
H(C2)	0·428	0·415	0·092
H(C3)	0·405	−0·205	0·076
H(C4)	0·526	0·120	0·129
H(C5)	0·485	−0·250	0·227
H(C6−1)	0·602	0·100	0·292
H(C6−2)	0·609	−0·250	0·290
H(O2′)	0·109	−0·085	0·157
H(O3′)	0·218	0·055	0·042
H(O6′)	0·501	0·380	0·412
H(C1′)	0·250	−0·330	0·292
H(C2′)	0·210	0·235	0·210
H(3′)	0·253	−0·250	0·154
H(C4′)	0·331	0·290	0·231
H(C5′)	0·354	−0·300	0·310
H(C6′—1)	0·460	−0·050	0·365
H(C6′−2)	0·428	−0·100	0·442
H(C7′−1)	0·270	−0·140	0·463
H(C7′−2)	0·192	−0·180	0·443
H(C7′−3)‡	0·225	−0·420	0·405
H(OW−1)	0·586	0·520	0·425
H(OW−2)	0·586	0·455	0·505

† The symbol in the parenthesis is the atom to which the hydrogen atom is bonded.

‡ The hydrogen coordinate was not located from three-dimensional difference Fourier syntheses.

Table 2. *Observed and calculated structure factors*

Columns are: Index, $|F_{\rm obs}|$, $|F_{\rm cal}|$, $A_{\rm cal}$, $B_{\rm cal}$.
* for unobserved reflections.

Index	$\lvert F_{\rm obs}\rvert$	$\lvert F_{\rm cal}\rvert$	$A_{\rm cal}$	$B_{\rm cal}$
H= 0 K= 0				
1	524	541	541	0
2	788	845	845-	0
3	204	182	182	0
4	892	930	930-	0
5	633	617	617	0
6	223	195	195-	0
7	221	245	245-	0
8	83	57	57-	0
9	217	188	188	0
10	189	170	170	0
11	35*	7	7	0
12	37*	23	23-	0
13	160	154	154	0
14	94	85	85-	0
15	144	168	168-	0
16	37*	22	22-	0
17	34*	39	39-	0
H= 2 K= 0				
0	284	277	277	0
1	607	607	607	0
2	597	620	620	0
3	445	452	452-	0
4	271	254	254	0
5	386	408	408	0
6	75	93	93	0
7	253	242	242	0
8	313	311	311	0
9	231	221	221-	0
10	54	54	54-	0
11	36*	22	22-	0
12	261	247	247-	0
13	290	279	279	0
14	251	253	253-	0
15	37*	52	52-	0
16	241	220	220	0
17	28*	7	7-	0
H= -2 K= 0				
1	395	366	366-	0
2	20*	4	4	0
3	282	257	257-	0
4	103	114	114-	0
5	63	52	52	0
6	1512	1659	1659-	0
7	249	254	254	0
8	1079	1094	1094	0
9	351	331	331	0
10	248	238	238	0
11	53	71	71-	0
12	202	192	192-	0
13	37*	11	11-	0
14	39*	64	64	0
15	290	277	277	0
16	337	350	350	0
17	36*	23	23-	0
18	32*	33	33	0
H= 4 K= 0				
0	237	253	253	0
1	110	108	108	0
2	71	75	75-	0
3	275	276	276-	0
4	424	431	431-	0
5	678	654	654-	0
6	274	289	289-	0
7	271	276	276-	0
8	167	172	172	0
9	39*	50	50-	0
10	357	348	348-	0
11	221	207	207-	0
12	79	84	84-	0
13	117	122	122	0
14	59	69	69-	0
15	71	48	48-	0
16	63	64	64	0
H= -4 K= 0				
1	111	105	105-	0
2	639	649	649-	0
3	630	590	590-	0
4	370	385	385	0
5	252	219	219-	0
6	885	893	893-	0
7	517	522	522	0
8	449	420	420	0
9	1100	1067	1067	0
10	250	245	245	0
11	51	56	56	0
12	521	506	506	0
13	229	246	246-	0
14	309	315	315	0
15	94	91	91-	0
16	266	280	280-	0
17	200	196	196	0
18	54	62	62	0
19	35*	66	66	0
H= 6 K= 0				
0	929	969	969-	0
1	42	62	62-	0
2	975	964	964-	0
3	458	469	469-	0
4	529	502	502	0
5	252	245	245-	0
6	429	411	411	0
7	319	322	322-	0
8	568	528	528	0
9	653	631	631	0
10	823	830	830-	0
11	618	603	603-	0
12	154	160	160-	0
13	141	133	133-	0
14	95	90	90	0
15	31*	23	23	0
H= -6 K= 0				
1	1046	1023	1023	0
2	527	520	520-	0
3	286	249	249-	0
4	554	531	531	0
5	89	62	62-	0
6	192	161	161	0
7	138	141	141	0
8	26*	6	6	0
9	56	17	17-	0
10	463	476	476-	0
11	522	468	468-	0
12	324	326	326	0
13	257	235	235-	0
14	185	149	149-	0
15	39*	25	25-	0
16	39*	23	23-	0
17	150	137	137	0
18	125	116	116-	0
19	65	58	58	0
H= 8 K= 0				
0	281	253	253-	0
1	933	926	926	0
2	1447	1433	1433-	0
3	1030	1005	1005-	0
4	525	499	499	0
5	117	106	106	0
6	295	279	279	0
7	224	230	230	0
8	121	88	88-	0
9	44*	54	54	0
10	338	317	317	0
11	39*	27	27	0
12	59	74	74	0
13	35*	16	16	0
14	31*	8	8	0
H= -8 K= 0				
1	262	208	208	0
2	171	187	187	0
3	516	492	492-	0
4	357	334	334-	0
5	1277	1250	1250-	0
6	545	540	540-	0
7	39	27	27-	0
8	183	207	207-	0
9	173	153	153-	0
10	171	165	165-	0
11	236	207	207-	0
12	128	137	137	0
13	36*	19	19	0
14	171	172	172-	0
15	153	165	165-	0
16	39*	24	24	0
17	38*	53	53-	0
18	144	155	155-	0
19	157	140	140	0
H= 10 K= 0				
0	42	52	52	0
1	525	533	533-	0
2	364	359	359-	0
3	292	280	280-	0
4	204	203	203-	0
5	180	167	167	0
6	211	211	211-	0
7	38*	27	27-	0
8	377	390	390	0
9	227	219	219	0
10	105	79	79-	0
11	37*	31	31-	0
12	34*	38	38	0
13	35*	65	65-	0
H=-10 K= 0				
1	103	81	81	0
2	214	173	173-	0
3	985	939	939	0
4	326	315	315	0
5	295	283	283	0
6	408	384	384	0
7	1184	1150	1150-	0
8	57	76	76	0
9	97	88	88	0
10	110	118	118	0
11	172	178	178	0
12	261	252	252-	0
13	249	235	235-	0
14	114	101	101-	0
15	305	303	303	0
16	94	101	101-	0
17	135	153	153-	0
18	33*	17	17-	0
19	102	93	93-	0
20	30*	35	35-	0
H= 12 K= 0				
0	883	880	880	0
1	383	359	359	0
2	162	153	153	0
3	94	78	78	0
4	73	43	43-	0
5	228	225	225	0
6	218	218	218-	0
7	128	115	115	0
8	39*	10	10-	0
9	124	126	126-	0
10	73	87	87	0
11	154	155	155-	0
H=-12 K= 0				
1	168	160	160	0
2	79	82	82	0
3	257	225	225	0
4	242	229	229	0
5	143	148	148-	0
6	210	189	189-	0
7	305	286	286	0
8	485	470	470	0
9	584	571	571-	0
10	33*	9	9-	0
11	289	277	277	0
12	457	437	437-	0
13	562	546	546	0
14	151	161	161-	0
15	635	625	625-	0
16	39*	38	38	0
17	126	112	112-	0
18	37*	2	2	0
19	82	94	94	0
20	30*	15	15-	0
H= 14 K= 0				
0	442	421	421	0
1	305	306	306-	0
2	99	84	84	0
3	76	72	72-	0
4	38*	27	27-	0
5	494	476	476	0
6	94	89	89	0
7	104	115	115	0
8	58	57	57-	0
9	34*	39	39	0
10	48	64	64	0
H=-14 K= 0				
1	117	114	114-	0
2	78	56	56-	0
3	280	307	307	0
4	32*	16	16-	0
5	64	91	91	0
6	86	90	90	0
7	32*	23	23-	0
8	38*	31	31-	0
9	185	179	179-	0
10	151	143	143-	0
11	73	72	72	0
12	58	66	66	0
13	38*	37	37-	0
14	61	64	64	0
15	564	534	534	0
16	128	136	136	0
17	91	74	74-	0
18	99	79	79	0
19	81	89	89-	0
20	30*	26	26	0
H= 16 K= 0				
0	59	41	41-	0
1	142	148	148-	0
2	38*	63	63-	0
3	106	121	121	0
4	39*	31	31	0
5	38*	22	22	0
6	37*	43	43-	0
7	152	150	150-	0
8	77	96	96-	0
H=-16 K= 0				
1	167	180	180-	0
2	135	122	122	0
3	85	92	92-	0
4	35*	33	33-	0
5	35*	17	17	0
6	105	84	84	0
7	275	269	269	0
8	132	130	130-	0
9	340	296	296	0
10	213	207	207	0
11	237	239	239	0
12	91	104	104	0
13	39*	44	44-	0
14	259	265	265	0
15	309	311	311	0
16	39*	44	44	0
17	113	107	107-	0
18	35*	12	12-	0
19	33*	54	54-	0
H= 18 K= 0				
0	253	236	236-	0
1	290	290	290	0
2	61	65	65	0
3	210	207	207-	0
4	58	37	37-	0
5	35*	53	53-	0
6	66	71	71	0
H=-18 K= 0				
1	226	238	238-	0
2	160	135	135	0
3	187	183	183-	0
4	441	434	434	0
5	472	495	495	0
6	499	489	489-	0
7	37*	47	47	0
8	113	105	105-	0
9	103	87	87-	0
10	38*	35	35-	0
11	161	170	170-	0
12	94	91	91	0
13	39*	51	51-	0
14	300	309	309	0
15	127	125	125	0
16	215	196	196-	0
17	33*	37	37-	0
18	54	75	75-	0
19	28*	12	12-	0
H= 20 K= 0				
0	92	93	93-	0
1	59	55	55-	0
2	57	52	52-	0
3	34*	70	70	0
4	76	56	56	0
H=-20 K= 0				
1	39*	60	60	0
2	39*	53	53-	0
3	39*	51	51-	0
4	408	411	411-	0
5	602	586	586-	0
6	233	240	240	0
7	384	379	379	0
8	227	220	220-	0
9	39*	9	9-	0
10	147	154	154-	0
11	269	273	273-	0
12	178	181	181	0
13	39*	24	24	0
14	38*	23	23-	0
15	37*	31	31	0
16	87	81	81-	0
17	156	155	155-	0
18	32*	29	29-	0
H= 22 K= 0				
0	136	124	124-	0
1	32*	16	16-	0
2	99	97	97-	0
H=-22 K= 0				
1	36*	29	29-	0
2	75	76	76	0
3	38*	43	43-	0
4	233	217	217-	0
5	105	110	110	0
6	145	145	145	0
7	39*	29	29-	0
8	39*	38	38	0
9	61	80	80-	0
10	38*	47	47	0
11	78	93	93	0
12	150	153	153-	0
13	163	167	167-	0
14	74	82	82	0
15	35*	36	36-	0
16	80	81	81	0
17	31*	11	11	0
H=-24 K= 0				
1	112	99	99	0
2	210	183	183-	0
3	30*	8	8-	0
4	54	36	36-	0
5	71	74	74	0
6	356	327	327	0
7	36*	34	34-	0
8	36*	17	17	0
9	36*	19	19-	0
10	73	85	85	0
11	35*	8	8-	0
12	358	332	332-	0
13	172	170	170-	0
14	52	54	54-	0
15	31*	21	21	0
H=-26 K= 0				
6	47	60	60	0
7	30*	38	38	0
8	31*	10	10-	0
9	129	141	141-	0
10	31*	42	42-	0
11	30*	11	11	0
12	190	186	186-	0
H= 1 K= 1				
0	1400	1428	1330-	520-
1	1714	1892	1891-	42
2	717	720	344	632-
3	465	487	484-	60-
4	501	496	26	495-
5	765	792	108	785-
6	308	311	165-	264-
7	303	287	60-	281
8	334	309	155	268
9	273	272	260	80
10	232	245	133-	206
11	352	331	232	236-
12	270	260	19	259-
13	197	189	171-	82-
14	61	68	11-	67
15	113	121	95-	75
16	95	85	82-	22
17	101	86	9	86
H= -1 K= 1				
1	1079	1157	1144	175
2	784	858	701	495
3	574	590	442-	391
4	318	306	301-	56
5	730	774	752-	183-
6	640	658	45	656
7	715	745	663	339-
8	735	737	736-	45-
9	195	192	122-	149
10	178	165	156-	56
11	360	368	277-	242
12	154	159	122	103-
13	152	160	136-	85
14	178	162	4-	162
15	38*	54	40	35-
16	138	154	144-	54
17	92	94	94-	3-
18	60	59	59	10
H= 3 K= 1				
0	640	634	204-	600
1	233	225	91	206-
2	598	615	196-	583
3	330	316	110	296-
4	414	429	411	125-
5	271	260	183-	185
6	214	216	214	26-
7	297	306	123-	280
8	204	233	116-	202-
9	173	164	136	92
10	158	159	159	10-
11	475	470	328	336-
12	79	84	46	70-
13	154	147	10	147-
14	77	89	64	62
15	133	143	143	8
16	50	38	14-	36-
H= -3 K= 1				
1	1626	1793	961-	1514
2	277	292	261	133-
3	375	391	384	77-
4	649	698	604-	350-
5	415	438	346	268-
6	310	320	83-	309
7	324	339	232-	247-
8	433	411	312-	268
9	81	106	84-	64-
10	171	157	91	128-
11	128	131	12	130
12	194	191	73-	177-
13	214	225	223-	30-
14	209	214	214-	13-
15	315	324	295-	134-
16	242	245	134	205-
17	117	136	134	20
18	113	107	43-	98
H= 5 K= 1				
0	528	518	515	55
1	288	263	249	83-
2	251	242	89	226-
3	607	592	0	592-
4	317	309	143-	274-
5	319	307	155-	265
6	275	296	292	52
7	301	325	27	324
8	129	127	108-	68
9	165	159	7-	159
10	543	549	463	296
11	237	217	211	49
12	137	141	136-	40
13	158	152	39	147-
14	41*	78	64-	45-
15	140	125	113	55
H= -5 K= 1				
1	768	808	92	803
2	560	572	266	506
3	1082	1168	1068	472-

Table 2 (*cont.*)

4	366	358	12	358-
5	821	875	603	635-
6	141	136	1-	136-
7	629	658	219-	621-
8	512	512	443-	256-
9	386	397	386-	93
10	302	333	312	117
11	245	259	21	258
12	107	112	33-	107-
13	169	147	57-	135
14	38•	48	47-	8-
15	39•	47	45	12-
16	38•	49	9	48
17	210	200	195-	44-
18	34•	36	21-	30
19	30•	40	39	9-
	H= 7 K= 1			
0	286	287	219-	186
1	557	558	123	544-
2	972	967	967	6
3	385	392	368	135
4	412	424	320-	279-
5	157	149	98	111-
6	99	112	94	62-
7	227	231	226	47
8	332	336	258	215-
9	618	618	617-	20-
10	137	124	115-	44-
11	232	220	217	34-
12	103	79	14	78
13	133	143	141	23-
14	50	48	15	45
	H= -7 K= 1			
1	551	528	425	314-
2	152	153	23	151
3	595	590	541	235-
4	240	245	41-	242-
5	503	508	20	508
6	305	303	295	69-
7	53	75	29	69
8	200	164	164	4-
9	509	509	187-	474
10	664	656	188	628
11	145	125	124	19
12	96	83	32-	77-
13	174	180	109	143-
14	152	139	61	125-
15	61	49	36-	34
16	137	126	25-	124-
17	37•	51	44	25
18	153	151	88	123
19	64	68	67	10-
	H= 9 K= 1			
0	377	358	104-	342
1	475	440	300-	323
2	295	285	263-	110-
3	499	510	505	71-
4	141	135	79	110-
5	82	88	83-	28-
6	149	162	102	126
7	277	271	237-	132
8	361	340	254-	226
9	263	270	184	199-
10	208	227	147	172-
11	183	166	153-	64
12	165	155	35	151-
13	124	110	105-	33
	H= -9 K= 1			
1	270	249	242	60-
2	591	611	371	485
3	374	370	370	5-
4	187	194	96	169
5	633	654	152-	636
6	293	300	282-	101-
7	414	397	320-	235-
8	600	614	483	379-
9	126	129	19	128
10	162	162	48	155
11	460	453	341	299-
12	116	119	107	52-
13	310	291	256	138
14	373	365	348	109-
15	94	90	31-	85-
16	162	156	108-	113-
17	192	204	159	126-
18	117	105	29-	101
19	32•	23	6-	22-
	H= 11 K= 1			
0	635	634	612-	166-
1	422	431	22-	431-
2	248	248	196	151-
3	297	280	36-	278
4	85	84	17-	82
5	146	138	36	134
6	306	314	75-	305
7	136	123	11	122
8	169	168	147-	81
9	187	189	151-	115-
10	110	111	62-	92-
11	82	80	73-	32
12	82	71	57-	42-
	H=-11 K= 1			
1	181	193	13-	193-
2	298	271	185-	199
3	431	436	433-	65-
4	346	328	289	155-
5	267	270	198-	184
6	685	691	548	421-
7	229	251	201	151
8	525	515	513-	47-
9	119	91	10	90-
10	249	249	248	19-
11	339	336	201	269-
12	468	495	485	97-
13	37•	13	12-	5
14	587	604	510-	324
15	128	128	126	21-
16	117	130	118	54-
17	124	117	23	115
18	36•	52	48	21
19	33•	51	7-	50
	H= 13 K= 1			
0	290	303	161-	257-
1	339	330	44	327-
2	231	242	132-	203-
3	75	68	68-	1-
4	165	133	133-	9
5	287	285	43-	282-
6	94	89	82	35-
7	61	71	69	15-
8	148	153	112-	104
9	35•	21	21-	2
10	32•	37	9-	36-
	H=-13 K= 1			
1	449	429	280-	325
2	185	200	185	76
3	381	371	245-	278
4	185	191	18-	190
5	75	79	75	23-
6	247	236	201-	123
7	521	542	444-	310-
8	301	279	76-	268-
9	204	205	120	166
10	249	247	201-	144
11	97	92	72	56
12	187	180	29-	177
13	282	298	86-	285
14	305	299	225	196
15	80	56	4	55-
16	297	308	304-	47-
17	59	65	32-	57-
18	73	72	53-	50-
19	33•	24	14-	19-
	H= 15 K= 1			
0	159	166	164-	24-
1	148	160	156-	35-
2	44•	75	71-	23-
3	117	108	10-	108
4	215	201	97	176
5	78	110	81	74-
6	38•	23	0	23-
7	36•	60	51	33
8	53	62	6	61-
9	30•	16	3	16-
	H=-15 K= 1			
1	441	454	304-	337
2	124	109	8	109-
3	151	148	75-	127-
4	235	232	1-	232
5	173	177	69	163
6	226	224	109-	195
7	94	103	2-	103-
8	71	116	56-	101-
9	35•	34	30	16-
10	184	178	65-	166-
11	221	212	212-	14
12	124	118	104-	56
13	127	108	103	32-
14	263	256	224-	124
15	303	304	198-	231-
16	152	150	31	147-
17	58	73	46-	57
18	35•	53	18	50-
19	32•	29	29	1-
	H= 17 K= 1			
0	78	75	68-	31-
1	209	210	205-	41
2	203	209	208	10-
3	126	138	114	78-
4	102	121	55-	108
5	36•	42	37-	21
6	102	98	98-	10
7	31•	38	17	34
	H=-17 K= 1			
1	239	250	70-	240
2	142	146	66	130-
3	442	467	407	229-
4	236	244	166	179-
5	193	193	176-	80-
6	186	185	139-	122
7	375	365	194	310-
8	76	96	96-	10-
9	164	167	165-	25-
10	166	160	81-	137-
11	38•	22	14-	17
12	79	91	32	86
13	138	146	104	103
14	178	164	163-	18-
15	292	289	283-	59
16	77	103	86	58-
17	36•	20	16-	11-
18	34•	30	26-	15-
19	48	69	57-	39-
	H= 19 K= 1			
0	307	305	286	107-
1	172	168	9	167-
2	58	79	77-	18-
3	133	122	60	106
4	101	105	96	43
5	48	54	18	51
	H=-19 K= 1			
1	39•	63	12-	62-
2	163	166	55-	156-
3	210	205	42	201-
4	252	243	185-	158
5	489	491	452	192
6	370	362	355	70
7	189	179	176-	32
8	117	127	104-	73
9	154	163	124-	106
10	163	197	152-	126
11	163	175	158	74-
12	222	220	65	210-
13	117	140	133-	46
14	78	58	28	50
15	113	93	42-	82
16	99	109	30	105
17	70	65	64	3
18	32•	43	38	21-
	H= 21 K= 1			
0	156	164	72-	147
1	54	59	32	50
2	113	111	107	29
3	60	63	18-	60
	H=-21 K= 1			
1	187	179	137	116-
2	38•	44	37-	25-
3	38•	58	26	52
4	300	297	296	14
5	266	264	34-	262
6	306	322	315-	67
7	162	146	63	132-
8	61	94	90	30
9	39•	24	14-	19
10	117	118	110	42-
11	182	192	31-	190-
12	38•	57	38	43-
13	202	193	152	119
14	145	150	116	95-
15	85	67	52	42
16	102	94	94	5-
17	32•	52	12	51-
	H= 23 K= 1			
0	72	95	82-	48
	H=-23 K= 1			
1	120	116	93-	69-
2	33•	62	60-	15-
3	70	78	69	36-
4	107	108	107	9
5	36•	34	24	24
6	58	60	47-	38-
7	89	83	43-	71
8	75	75	74	9
9	58	82	61	55-
10	160	154	60-	142-
11	151	148	24-	146-
12	222	219	203	82-
13	84	95	28	91
14	126	119	33	115
15	77	76	50	56
16	91	86	54-	67
	H=-25 K= 1			
4	97	80	49-	63-
5	63	66	65-	7-
6	50	63	3	63-
7	32•	56	14-	54
8	78	75	27-	70
9	78	79	33-	72
10	32•	26	1-	26
11	32•	20	13	15-
12	178	153	145	50
13	83	85	76	38
	H= 0 K= 2			
0	1102	1114	682	882-
1	645	659	179-	634
2	421	396	395-	30-
3	356	375	206	314-
4	346	348	34	347
5	371	373	306	213-
6	675	689	577	377-
7	379	393	222-	325-
8	234	242	105-	218
9	216	235	112	207
10	178	157	114-	109
11	165	178	71	164
12	183	196	6-	196
13	169	179	123	129-
14	241	235	207	110-
15	108	97	96	15
16	66	51	51	3-
	H= 2 K= 2			
0	285	277	264-	83-
1	426	413	165	379
2	602	601	469	377-
3	30•	57	37-	44
4	187	214	106	186-
5	287	278	200-	192-
6	268	251	136-	211
7	224	227	196	115
8	236	223	217-	51
9	205	193	186-	51
10	208	202	111-	168-
11	195	216	188-	106-
12	162	170	137-	101
13	174	168	6-	168-
14	57	42	2-	42
15	53	42	35-	22
16	29•	22	11	19
	H= -2 K= 2			
1	307	334	8-	334-
2	635	626	588	214-
3	393	375	321	193
4	576	588	337	482
5	320	315	315	1-
6	403	404	108-	390
7	375	370	332	163
8	212	217	214	36-
9	166	160	38-	156-
10	149	156	144	60-
11	59	59	59	8-
12	116	81	24-	77
13	210	212	208	45-
14	280	298	174	242-
15	76	80	73	32-
16	106	110	95	56
17	148	162	124-	104
	H= 4 K= 2			
0	413	377	85-	369
1	268	270	127-	239
2	331	331	322	76-
3	68	40	38	14
4	250	213	156	146-
5	94	102	19	100
6	171	158	54	149-
7	34•	34	4-	33
8	109	114	38-	108
9	76	91	49-	77-
10	136	124	103-	70-
11	146	132	20	130
12	194	181	98-	152
13	111	110	110-	7-
14	69	66	65-	15-
15	157	143	93-	108-
	H= -4 K= 2			
1	399	389	364	137
2	387	394	261-	295
3	166	146	113-	93
4	433	408	377-	155-
5	415	396	114-	379-
6	236	218	155	154-
7	161	172	70-	157-
8	163	137	6	137
9	117	96	66-	69-
10	171	150	141-	50
11	36•	51	51-	5
12	125	123	112	51-
13	215	201	144	139
14	268	291	171	235-
15	104	103	48	91
16	190	189	186-	34
17	190	171	14	170-
	H= 6 K= 2			
0	249	249	105-	225
1	602	604	423-	431-
2	475	464	231-	402-
3	154	164	163	15
4	189	166	58-	156
5	338	345	186-	290
6	295	300	218-	206-
7	294	322	272-	171
8	38•	19	19	1
9	230	234	228	55-
10	146	151	15-	151
11	134	111	93-	60-
12	120	123	81	93-
13	62	67	47-	49
14	73	63	58	25-
	H= -6 K= 2			
1	647	646	121-	634-
2	547	555	502-	238
3	889	887	712-	529
4	682	660	644-	143
5	92	94	27-	90-
6	317	308	162	262-
7	162	143	122	75-
8	197	202	26-	200
9	131	124	62	107-
10	217	208	153	140-
11	226	218	45	214
12	124	122	35	117-
13	136	138	53-	128
14	39•	17	13	10
15	42•	38	10	36-
16	162	171	86	148
17	105	104	80	67
18	63	89	85-	28
	H= 8 K= 2			
0	245	242	78-	229
1	416	400	379	128-
2	574	554	66-	550
3	411	415	402-	104-
4	327	315	10-	315-
5	41•	73	7-	73
6	210	214	12	214-
7	151	172	87	148-
8	247	252	248-	42-
9	231	246	236-	70
10	151	152	149	28-
11	57	77	73	25-
12	53	24	14	19-
13	30•	27	13-	24
	H= -8 K= 2			
1	173	154	103-	115-
2	350	338	317-	119-
3	663	631	521-	355
4	215	204	87-	184
5	466	456	386	242-
6	405	392	206	333-
7	176	184	174	60
8	114	98	94	27
9	101	94	36-	87-
10	105	105	91	53-
11	560	560	306-	469
12	334	349	248-	246
13	168	176	142-	104-
14	222	217	152-	154-
15	127	121	33	117-
16	37•	27	25-	12-
17	72	71	33-	63-
18	32•	53	52-	10-
	H= 10 K= 2			
0	188	191	189	24
1	91	93	50	79-
2	195	225	188	123-
3	420	408	368	177-
4	219	218	173-	133
5	77	65	10	64
6	207	208	38	205
7	94	156	106	114
8	308	316	299	103-
9	37•	40	38-	9-
10	35•	39	31-	24-
11	115	109	57	94-
	H=-10 K= 2			
1	179	171	155-	74
2	198	188	178-	62
3	93	67	14-	66
4	93	102	28	98
5	182	170	96	141-
6	189	192	178	72-
7	445	456	300-	344
8	368	357	150-	323-
9	372	384	295	246-
10	240	251	158-	194-
11	463	469	464-	72
12	451	474	449-	153
13	346	343	338-	58-
14	155	151	138	63
15	196	184	165	81-
16	103	96	75-	60
17	56	48	33-	34-
18	89	77	4	77-
	H= 12 K= 2			
0	241	250	58-	243-
1	143	156	22-	155
2	45•	35	34-	8-
3	124	120	73	96-
4	174	176	26-	174
5	145	166	155-	61
6	106	105	42-	96
7	252	277	152	232-
8	197	187	168	82-
9	143	136	77	114
10	31•	30	19	23-
	H=-12 K= 2			
1	162	180	95	153-
2	300	293	292	9
3	80	54	41-	35
4	91	85	22-	82-
5	139	139	56-	127-
6	362	373	195-	318-
7	247	248	244	41-
8	349	357	348	82
9	266	290	177-	229
10	120	139	138-	12-
11	262	263	251-	78
12	411	430	155-	401
13	479	505	401	306-
14	210	222	194	107-
15	168	163	120-	110
16	102	103	50	90-
17	141	142	139	28-
18	33•	59	55	22-
	H= 14 K= 2			
0	452	469	302	359-
1	173	205	47	200
2	61	75	34-	67-
3	154	148	74	128-
4	39•	59	50-	31
5	143	134	127-	40
6	181	177	122-	128
7	106	107	67-	83-
8	66	63	40	50
	H=-14 K= 2			
1	486	472	409	235-

Table 2 (*cont.*)

2	196	194	188	45
3	280	284	19-	284
4	321	317	46	313
5	134	125	78-	98
6	250	240	239	23
7	195	197	130	148
8	129	126	30-	123-
9	369	353	211	283-
10	77	98	59	78
11	105	90	84	34
12	146	130	83	101
13	39•	34	22	26-
14	128	135	13-	135-
15	78	77	74	22-
16	121	113	76	84
17	35•	24	5	23-
18	134	127	63	111-
H= 16 K= 2				
0	301	289	289	10-
1	184	177	2	177
2	93	97	28-	93
3	60	63	27	57
4	58	66	40	52-
5	35•	42	22-	35
6	67	74	5	74
7	47	39	17-	35-
H=-16 K= 2				
1	353	365	349	107-
2	105	86	82	26-
3	227	265	233-	128
4	294	320	314-	61-
5	38•	41	41-	6
6	103	115	67	93
7	91	81	79-	20-
8	78	76	41-	64
9	269	265	91	249-
10	93	86	85	14
11	146	154	132	78
12	39•	36	35	7
13	61	69	68-	11
14	61	52	15	50-
15	59	49	48	11-
16	36•	54	9	53-
17	102	94	71	61-
18	49	41	34	23-
H= 18 K= 2				
0	44•	39	39-	6-
1	177	185	161	91-
2	128	128	14-	127-
3	164	168	166-	23-
4	52	27	2	27
5	131	121	62-	104
H=-18 K= 2				
1	79	124	68-	104-
2	215	223	220-	35-
3	500	512	339-	384
4	79	83	31	77
5	258	258	60	251-
6	290	297	269-	127
7	162	163	161-	26-
8	155	154	153	12
9	278	299	280	103-
10	222	231	216	80-
11	39•	49	39	29-
12	190	173	171-	27-
13	248	235	10	235
14	37•	77	70	33
15	57	58	8-	57
16	103	96	52	80
17	65	66	47	46-
H= 20 K= 2				
0	123	119	3-	119-
1	209	194	189-	44
2	179	171	5-	171
H=-20 K= 2				
1	144	131	49	121-
2	76	72	60-	40
3	77	79	58	54
4	134	129	108-	71
5	126	131	130-	14-
6	105	93	89	27-
7	105	121	116	32
8	116	111	23	109
9	212	208	164	128-
10	60	65	5-	65-
11	349	358	168-	316
12	59	51	43	27
13	152	143	75-	121-
14	85	83	80-	20-
15	34•	12	6-	10-
16	76	77	74-	21-
H= 22 K= 2				
0	29•	15	15	3
H=-22 K= 2				
1	31•	20	19-	6-
2	33•	34	32	11-
3	34•	24	23	3-
4	55	63	44-	45
5	85	88	77	43-
6	73	82	36-	74
7	118	147	127-	75
8	164	170	12	169-
9	157	139	55-	128-
10	73	79	41-	67-
11	72	79	70-	36
12	180	166	162-	38
13	53	55	42-	35
14	65	56	46-	33
15	132	129	126-	28
H=-24 K= 2				
5	30•	26	26	0
6	93	96	64-	71-
7	118	115	62-	96
8	32•	35	35-	3-
9	31•	32	13	29
10	31•	37	25	26-
11	48	57	49-	28-
12	30•	51	10	50
H= 1 K= 3				
0	523	496	419-	265
1	461	458	386-	247
2	105	123	80-	93-
3	251	239	13	238
4	305	310	308	34
5	55	50	8	50-
6	397	430	423-	78-
7	225	212	175-	121
8	91	89	57	68
9	93	114	27-	111-
10	170	178	36-	174
11	93	86	17	84-
12	90	82	78	25-
13	85	115	63	96
14	98	94	85	39-
H= -1 K= 3				
1	193	180	116	137-
2	432	430	420-	91-
3	159	146	125-	75
4	232	235	166	166-
5	338	328	253-	209
6	277	288	279	71
7	374	390	61	385-
8	76	78	39-	68-
9	144	156	88	129-
10	154	159	122-	102
11	39•	25	25	2-
12	105	107	52	94-
13	89	80	73-	34
14	123	115	115-	3
15	126	114	110-	28
H= 3 K= 3				
0	255	244	243	21
1	66	44	33-	29
2	52	28	14	24
3	266	238	203-	125
4	145	129	58	115-
5	254	235	94	215
6	58	54	18-	51-
7	142	152	114	100-
8	105	95	92-	21-
9	146	149	113	98-
10	39•	36	17	34-
11	149	162	73-	144-
12	254	235	219	88
13	168	156	16	155
14	97	88	38-	79
H= -3 K= 3				
1	105	86	64	57-
2	663	665	413-	521-
3	566	558	252	498-
4	281	269	236	128
5	177	178	163	73-
6	187	186	166	84
7	317	309	309-	9-
8	235	238	25	237
9	298	311	264-	164
10	357	388	365-	130-
11	128	133	130	27-
12	94	98	80-	56-
13	115	102	88-	51
14	144	161	38-	157
15	159	151	143-	47
16	125	120	39	113-
H= 5 K= 3				
0	219	222	57	215-
1	147	158	129	91
2	103	86	70	50
3	147	132	39-	126-
4	379	387	386	23-
5	371	378	362	108
6	77	112	110-	22-
7	39•	33	25	22
8	155	158	145-	62-
9	39•	17	10-	14
10	219	234	194	131-
11	98	92	4	92-
12	163	151	150	19
13	104	111	99	49-
H= -5 K= 3				
1	137	139	133-	38
2	240	244	213-	119
3	223	227	86	210-
4	389	376	156	344
5	54	39	37	13-
6	71	72	9-	72
7	187	208	102-	181
8	111	148	120	88
9	91	112	11	109
10	160	168	109-	128-
11	163	156	122-	96-
12	210	197	179-	84-
13	38•	50	36	35
14	75	86	31-	81
15	123	145	138	42
16	126	140	137	27
H= 7 K= 3				
0	70	86	67	54-
1	106	82	54-	61-
2	329	319	317	36-
3	377	339	131	313
4	292	303	238-	186
5	104	110	7-	110-
6	209	204	189-	77
7	39•	31	21-	23
8	201	195	193	27
9	257	255	7-	255
10	85	96	55-	79-
11	67	69	26	63-
12	71	69	67	14
H= -7 K= 3				
1	218	211	197-	76-
2	128	132	98	88
3	480	456	409	201-
4	299	270	268	32
5	95	92	85	36-
6	235	246	215-	120
7	127	129	124	37
8	121	145	88	115-
9	209	205	83-	187
10	188	189	16	189-
11	170	189	36	186-
12	216	220	196	101-
13	161	143	137	40-
14	37•	42	9	41
15	117	120	112	45
16	52	32	9-	31-
H= 9 K= 3				
0	294	306	239	192
1	230	248	224	107
2	202	191	147-	122-
3	409	406	249	320-
4	202	202	198	36
5	45•	73	42	59-
6	190	181	62-	170-
7	327	322	317-	58
8	167	187	26-	185
9	158	143	48	135
10	77	78	78-	5
H= -9 K= 3				
1	263	250	249-	4-
2	207	236	235	17
3	230	225	2-	225-
4	226	228	151-	171-
5	229	246	162	186
6	110	94	93-	15
7	275	281	281	10
8	258	258	235	105-
9	159	157	125-	95
10	79	71	62-	35-
11	146	152	37-	148-
12	163	164	128	103
13	213	216	129	174
14	76	53	53-	3
15	36•	12	7-	10-
16	80	63	9	62
17	47	31	21	22-
H= 11 K= 3				
0	282	282	103	262
1	44•	68	65	19
2	106	100	97-	25
3	79	80	55-	59-
4	39•	13	3-	12-
5	105	97	80	54-
6	46•	29	12	26-
7	176	185	162-	88-
8	81	62	1-	62-
9	31•	27	17	21-
H=-11 K= 3				
1	157	146	37	141
2	76	72	71-	9-
3	276	275	274-	14
4	295	268	112-	244-
5	216	219	194-	103
6	102	93	90-	26
7	375	374	314	204
8	379	387	248-	297
9	196	193	193-	15-
10	146	179	172	49
11	147	154	148	44
12	353	340	263	216-
13	116	103	86-	57-
14	140	142	121-	74
15	117	126	104	71-
16	156	138	125	60
17	61	52	41	32
H= 13 K= 3				
0	310	316	173-	267
1	94	124	114	48-
2	117	129	53-	118
3	126	107	57-	45
4	59	53	36	39-
5	74	48	6	48-
6	70	63	53	34-
7	127	127	124-	27
H=-13 K= 3				
1	381	377	318-	202
2	366	360	299-	200-
3	38•	40	0	40
4	144	155	32	151-
5	60	65	64-	14-
6	78	73	61	39
7	127	118	87-	79-
8	184	172	120	124-
9	286	272	266	56
10	185	194	4	194
11	163	158	44	151-
12	196	195	100-	167-
13	306	289	282-	65-
14	58	62	62	8
15	84	73	66	32
16	106	101	18-	99
H= 15 K= 3				
0	61	75	75-	9-
1	166	158	158	4
2	59	68	58	36-
3	119	123	123-	4
4	34•	48	46-	14
5	147	136	107-	83-
6	47	22	5	21-
H=-15 K= 3				
1	39•	30	16	25
2	286	272	118-	245-
3	128	138	14	137-
4	162	165	165	9-
5	118	110	107-	28
6	39•	35	2	35-
7	61	62	1	62-
8	163	170	25-	169
9	94	98	66-	72
10	106	88	85-	24
11	93	99	68	72-
12	158	148	112-	98-
13	174	164	158-	44-
14	125	127	12-	126
15	147	153	127-	84
16	31•	40	39-	6-
H= 17 K= 3				
0	166	177	175-	31-
1	96	79	34-	71
2	147	151	139	59-
3	104	106	50-	94-
4	122	121	44	113-
H=-17 K= 3				
1	102	117	26	115
2	124	150	27	148
3	233	226	209	85-
4	60	52	16-	50-
5	264	289	287-	31-
6	38•	53	53	1
7	105	95	92	22-
8	136	130	93	91
9	92	97	58-	78
10	220	216	199-	84-
11	102	109	96-	50-
12	88	99	37-	91
13	56	59	13-	58-
14	110	97	82-	51
15	125	109	8	108
H= 19 K= 3				
0	168	160	145	67-
1	35•	63	11-	62-
H=-19 K= 3				
1	164	164	48	156
2	175	163	117	113
3	148	146	70	129-
4	118	106	102-	30
5	119	111	48	100-
6	110	120	73	95-
7	56	63	63-	4-
8	57	48	22-	42-
9	109	91	89-	20
10	163	155	85	129
11	272	255	243	78-
12	135	152	18-	151-
13	33•	41	40-	7
14	49	37	26-	26-
H=-21 K= 3				
2	148	136	120	62
3	128	103	91	50-
4	125	116	18	114-
5	66	72	67	26-
6	79	74	59-	45
7	108	109	50	97-
8	52	40	1	40-
9	154	151	64-	136
10	114	140	140	12
11	31•	30	19	23
12	73	81	2-	81
H= 0 K= 4				
0	407	400	173	361-
1	221	225	204	95-
2	193	183	60	173
3	92	98	40-	90
4	116	107	55-	92
5	294	299	207	215
6	146	147	139	48-
7	162	156	156-	7-
8	38•	45	38-	24
9	132	134	13	134-
10	74	79	77	17
11	94	73	54	48-
12	64	35	5	35-
H= 2 K= 4				
0	227	228	3-	228-
1	424	420	407	104-
2	126	119	118	16-
3	304	278	185	207
4	184	199	160-	118-
5	248	243	234-	65
6	184	195	69	182
7	93	81	57	58-
8	38•	11	6	8
9	74	78	78-	6-
10	105	98	19-	97
11	152	133	36	128
H= -2 K= 4				
1	228	221	126-	181-
2	194	186	120	143
3	144	159	137-	80
4	44•	74	33-	66-
5	106	96	86-	42-
6	178	193	165-	99
7	107	96	24	93
8	127	142	22-	141-
9	206	212	23	211-
10	305	305	305	7-
11	36•	20	3-	20
12	91	109	36-	102
13	108	88	81	34
H= 4 K= 4				
0	206	213	134-	165-
1	105	101	15-	100-
2	117	109	67-	86-
3	215	198	29	196
4	210	197	179-	83-
5	146	139	85	110-
6	136	132	131	13-
7	60	46	3	46-
8	58	50	13	49-
9	230	197	182-	76-
10	206	200	181-	86
11	139	140	4-	140
H= -4 K= 4				
1	174	203	178-	98-
2	240	252	103	230
3	105	90	90-	3-
4	39•	57	19-	54
5	79	83	44-	70
6	204	199	50	192
7	198	182	163	82
8	273	275	107	253-
9	145	141	141	16-
10	114	116	11-	115
11	152	151	149-	27-
12	40•	63	58	24
13	120	113	112	11
H= 6 K= 4				
0	61	64	56-	31
1	267	273	211-	173
2	94	122	122-	9
3	232	219	212	53
4	79	137	71	118
5	126	132	121-	53-
6	59	63	47-	42-
7	74	65	18	62-
8	206	191	8-	191-
9	105	120	62	102-
H= -6 K= 4				
1	44•	59	51-	29
2	230	225	194	115
3	94	104	53	90-
4	154	148	143-	36
5	146	159	135-	83
6	107	116	42	108
7	39•	56	27	49-
8	106	102	21-	100-
9	38•	42	6-	42-
10	60	72	9	71-
11	160	138	117	73
12	106	96	96-	16-
13	38•	51	31-	40-
14	30•	20	10-	17
H= 8 K= 4				
0	210	218	149-	159-
1	162	160	159-	11-
2	321	311	28	310
3	319	293	275-	99
4	91	92	57-	72-
5	112	91	90	13-
6	97	112	79	79
7	192	180	179	11-
8	118	130	31-	126-
H= -8 K= 4				
1	79	95	71	63-
2	177	171	92-	144-
3	117	104	100-	28-
4	147	141	105	93
5	138	133	33	129-
6	39•	18	16	8
7	62	67	64-	21-
8	197	205	164-	124-
9	105	87	87-	8-
10	178	167	161-	42-
11	110	124	54	112
12	55	51	16-	48-

Table 2 (*cont.*)

13	67	52	34-	40-
14	62	90	19	88
H= 10 K= 4				
0	183	178	105	143-
1	135	136	73-	115-
2	204	186	84	166
3	112	104	94-	45
4	73	81	74-	31
5	191	174	108-	136-
6	32*	30	1-	30-
7	82	89	62	64
H=-10 K= 4				
1	106	130	130	13
2	184	170	131-	108-
3	128	116	101	57-
4	45*	75	21-	72-
5	62	76	75-	10
6	118	125	70	104
7	93	121	115-	36
8	78	82	82-	0
9	166	160	156	37
10	76	68	8	67
11	57	65	36	55
12	95	74	18-	72-
13	89	77	64-	43
14	82	93	58	73
H= 12 K= 4				
0	113	108	101-	38-
1	37*	35	20	28-
2	126	133	94	94
3	70	58	17	55
4	79	62	43	44
5	48	37	2-	37-
H=-12 K= 4				
1	133	113	98	57-
2	222	234	233	8-
3	135	134	82	106
4	78	61	35-	49-
5	135	125	96	79
6	78	71	69-	15
7	134	124	31	120-
8	157	153	140	62
9	131	115	68-	93
10	165	167	131-	104-
11	72	103	77-	69-
12	69	59	38	45
13	37*	24	15	19-
H= 14 K= 4				
0	84	70	32	62-
1	69	74	70	24-
2	88	99	59	80
3	100	105	104	9
H=-14 K= 4				
1	36*	19	15-	11-
2	74	82	58-	58
3	58	47	39-	26-
4	161	149	10-	148-
5	101	93	91	16
6	101	77	2-	77-
7	58	67	13-	66
8	110	104	73-	73
9	134	124	22-	122-
10	203	192	190	28
11	92	75	73-	15-
12	37*	51	29	42
13	48	54	50	20
H= 16 K= 4				
0	36*	32	26	19
H=-16 K= 4				
1	51	53	53-	3-
2	38*	34	25	23
3	34*	23	16-	16-
4	34*	32	26-	18-
5	180	164	141	83
6	94	94	86	39
7	34*	27	11	25
8	34*	45	43	15-
9	101	84	83-	13-
10	122	145	23-	143
11	31*	19	10-	17
12	81	74	73	9
H=-18 K= 4				
3	60	44	22	39
4	120	105	78	70
5	74	51	51-	9
6	93	94	91-	24
7	31*	38	37-	12
8	30*	45	44	11-
9	119	109	79	74
H= 1 K= 5				
0	89	95	19-	93
1	121	129	123-	36
2	120	98	54-	81-
3	87	91	87	28
4	106	81	54	60
5	70	87	24	84-
6	90	129	126-	27-
7	64	50	36	34
8	139	142	142	4-
H= -1 K= 5				
1	58	43	28	32
2	37*	34	14	31-
3	42*	86	47	72-
4	143	134	131-	24-
5	132	125	125-	5
6	82	45	41	20-
7	38*	27	20	19
8	40*	54	22	49
H= 3 K= 5				
0	129	120	39	114
1	119	100	95-	32
2	163	165	115-	119-
3	96	103	64-	81-
4	190	177	162-	71
5	38*	50	12	49
6	76	62	24	57-
7	42*	40	38	14-
H= -3 K= 5				
1	137	147	124	78
2	37*	45	35	27
3	88	78	77-	10
4	42*	42	40-	12
5	41*	51	29-	43-
6	130	132	57	120-
7	68	62	53-	33-
8	65	79	1	79
9	61	79	71-	36
H= 5 K= 5				
0	156	136	104	87
1	116	92	71	59
2	83	90	89-	16
3	148	141	128-	59-
4	66	61	21	57-
5	46*	91	66	63
H= -5 K= 5				
1	238	224	224	8-
2	170	166	89	139-
3	205	187	151-	110-
4	108	105	104	8-
5	72	60	48	36-
6	94	81	8	81-
7	60	74	54-	51
8	120	114	78-	83
9	91	119	111	44-
H= 7 K= 5				
0	94	121	72	97
1	102	97	96	15-
2	116	137	83	109-
3	43*	61	54	29-
4	44*	57	57-	8
H= -7 K= 5				
1	35*	23	23	2-
2	55	47	45	16-
3	40*	44	42	13
4	159	134	104	85-
5	70	78	64-	44-
6	39*	79	66-	44
7	79	88	87-	12
8	112	121	95-	75
9	119	143	116	84
H= 9 K= 5				
0	106	60	28-	54
1	42*	57	25	51
2	91	63	55-	31-
H= -9 K= 5				
1	116	102	97-	33-
2	151	139	92	104-
3	33*	40	35-	20-
4	152	149	109-	102
5	100	82	66	49
6	33*	34	30-	16
7	50	54	26-	47
8	63	92	22	89
H=-11 K= 5				
1	106	112	107	32-
2	63	68	12-	67
3	102	79	7-	79
4	49	44	7	43
5	36*	79	76	21-
6	63	39	4	39-
7	61	37	22	30

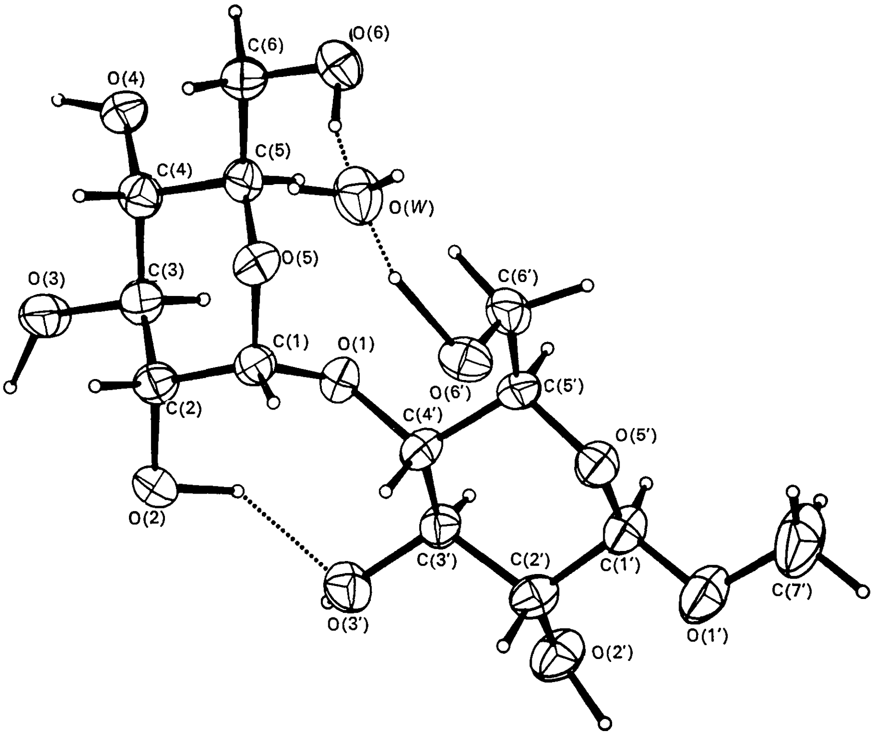

Fig. 1. The structure of one asymmetric unit of methyl β-maltopyranoside monohydrate. Dotted lines are intramolecular hydrogen bonds. The diagram is produced by ORTEP (Johnson, 1965).

O(6')H, on the other side of the molecule. Therefore, the molecule with its associated water forms a relatively rigid four-ring system. Only the hydrogen bond linking O(2) and O(3') was observed in the cyclohexaamylose complex (Hybl *et al.*, 1965). There are two intramolecular hydrogen bonds in the crystal structure of sucrose [O(1')-O(2) and O(5)-O(6')] (Brown & Levy, 1963) and one in cellobiose [O(5)-O(3')] (Brown, 1966). The packing of the molecules in the crystal appears to be determined mainly by the hydrogen bonds, of which there are nine per asymmetric unit, as illustrated in Fig. 2. Each of the oxygen atoms in the molecule, except the ring oxygen atoms, O(5) and O(5'), and the bridge oxygen atoms, O(1) and O(1'), is associated with

Table 3. *Principal axes of thermal ellipsoids*

The root mean square displacement U_i corresponds to the ith principal axis of the ellipsoid, and θ_{ia}, θ_{ib}, θ_{ic} are angles between the ith axis and the crystallographic axes a, b, c respectively. The B_i are equal to the corresponding $8\pi^2U_i^2$.

	i	B_i	U_i	θ_{ia}	θ_{ib}	θ_{ic}
O(1)	1	1·971 Å^2	0·1580 Å	28·6°	83·0°	144·5°
	2	1·986	0·1586	97·1	151·2	110·9
	3	2·987	0·1945	62·5	117·7	62·7
O(2)	1	1·846	0·1529	70·2	120·8	56·8
	2	3·038	0·1976	159·4	95·6	43·2
	3	4·361	0·2350	84·5	31·4	65·7
O(3)	1	2·067	0·1618	101·0	91·0	16·3
	2	2·516	0·1785	146·0	57·5	75·8
	3	6·248	0·2813	58·3	32·6	97·8
O(4)	1	2·069	0·1619	30·8	120·4	117·0
	2	3·018	0·1955	79·2	64·0	150·2
	3	3·983	0·2246	61·6	42·0	78·4
O(5)	1	1·739	0·1484	65·7	54·5	64·2
	2	2·303	0·1708	153·3	65·9	54·9
	3	3·270	0·2035	100·3	134·7	46·1
O(6)	1	2·245	0·1686	84·8	105·8	35·9
	2	3·184	0·2008	111·1	154·9	91·9
	3	3·846	0·2207	21·8	109·0	125·8
C(1)	1	1·981	0·1584	77·5	14·1	101·5
	2	2·216	0·1675	167·4	77·4	63·3
	3	2·950	0·1933	88·4	83·8	29·5
C(2)	1	1·938	0·1567	56·2	142·6	118·0
	2	2·676	0·1841	73·6	63·0	151·7
	3	2·917	0·1922	38·6	66·2	86·2
C(3)	1	1·826	0·1521	110·4	29·6	61·9
	2	2·490	0·1776	59·9	60·8	149·8
	3	3·189	0·2009	37·7	85·8	79·8
C(4)	1	2·234	0·1682	68·6	21·4	99·9
	2	2·790	0·1880	126·6	76·8	114·3
	3	2·874	0·1908	44·4	106·5	153·6
C(5)	1	1·971	0·1580	38·5	55·7	126·5
	2	2·505	0·1781	123·1	65·5	113·3
	3	3·409	0·2078	107·4	44·5	45·6
C(6)	1	2·181	0·1662	36·1	99·4	82·3
	2	3·003	0·1950	54·4	68·3	155·5
	3	4·261	0·2323	95·2	23·8	66·9
O(1′)	1	2·306	0·1709	25·6	90·9	142·8
	2	3·555	0·2122	114·9	104·6	125·6
	3	6·302	0·2825	95·5	14·7	99·5
O(2′)	1	1·900	0·1551	39·5	77·2	79·8
	2	3·459	0·2093	50·7	99·8	164·0
	3	5·574	0·2657	93·8	16·2	102·2
O(3′)	1	1·779	0·1501	68·1	89·1	49·1
	2	3·232	0·2023	139·4	124·8	51·2
	3	4·732	0·2448	57·7	145·2	115·0
O(5′)	1	2·160	0·1654	78·7	83·4	39·2
	2	2·519	0·1786	167·5	93·9	51·0
	3	3·728	0·2173	95·1	7·7	92·7
O(6′)	1	2·437	0·1757	54·0	84·3	63·6
	2	2·869	0·1906	82·4	172·3	92·1
	3	4·224	0·2313	37·0	84·8	153·5
C(1′)	1	2·118	0·1638	23·9	90·1	141·1
	2	2·426	0·1753	110·6	119·8	123·0
	3	3·762	0·2183	78·5	150·2	71·8

Table 3 (*cont.*)

	i	B_i	U_i	θ_{ia}	θ_{ib}	θ_{ic}
C(2′)	1	2·610	0·1654	28·2	86·7	89·3
	2	2·729	0·1859	67·4	131·6	138·3
	3	3·646	0·2149	105·9	138·3	48·3
C(3′)	1	1·642	0·1442	37·2	76·2	82·6
	2	2·282	0·1700	60·6	73·7	163·3
	3	3·555	0·2122	69·3	158·4	104·9
C(4′)	1	1·829	0·1522	11·9	97·6	126·0
	2	2·208	0·1672	101·7	119·1	131·5
	3	3·071	0·1972	92·1	149·7	62·3
C(5′)	1	1·746	0·1487	32·8	122·8	112·3
	2	2·815	0·1888	76·4	69·2	155·8
	3	2·914	0·1921	60·8	40·4	81·1
C(6′)	1	2·049	0·1611	95·5	95·2	22·4
	2	3·005	0·1951	132·2	42·2	71·9
	3	3·769	0·2185	42·7	48·3	102·7
C(7′)	1	2·639	0·1838	124·8	97·1	10·5
	2	4·313	0·2337	141·0	103·6	99·3
	3	10·704	0·3682	74·8	164·6	95·0
O(*W*)	1	2·824	0·1891	82·0	88·6	35·3
	2	3·305	0·2046	135·7	133·5	64·4
	3	5·130	0·2549	46·8	136·4	112·5

two hydrogen bonds, one as donor and one as acceptor, while the water molecule has four hydrogen bonds in distorted tetrahedral configuration, two donor and two acceptor. The water molecules and the oxygens O(6′) are joined in a closed four-membered ring of hydrogen bonds around the twofold axes. These closed rings form stacks along the axis which are linked by the hydrogen bonds between the water molecules and the other primary alcoholic oxygen atoms, O(6). The other hydrogen bonds form helical chains extending in the *b*-axis direction with 3 and 4 hydrogen bonds per repeat unit of the helix. The 4-unit helices link the atoms O(2) and O(3′) and their symmetry relations around the twofold screw axes. These helices are right-handed with the donor–acceptor sequence O(2)→O(3′)→O(2)→O(3′). The hydroxyls at O(2′), O(3), O(4) and their translational relations form the 3-unit helices. These helices are left-handed with the sequence O(2′)→O(3)→O(4). Thus there is a tendency for the polarity resulting from these helices of polar bonds to be balanced in the polar direction of the crystal. In this structure, however, there are twice as many 3-unit left-handed helices as 4-unit right-handed ones. Similar helices of hydrogen bonds have been observed in other carbohydrate structures. In methyl-1-thio-β-D-xylopyranoside, which is triclinic $P1$, there are two symmetry unrelated 3-unit helices with opposite senses (Mathieson & Poppleton, 1966). In methyl-α-glucose (Berman & Kim, 1967), there are left and right-handed 3-unit helices by reason of the non-polar space group, $P2_12_12_1$. Similarly, in α-methyl-D-galactoside-6-bromohydrin (Robertson & Sheldrick, 1965) the 6-unit helices which spiral around the screw axes are paired in opposite senses by the space group symmetry. All the available hydrogen atoms of the hydroxyl groups are used in hydrogen bond formation. The hydrogen atom H(O6′) was observed closer to O(*W*) than to O(6′) by 1·29 *versus* 1·54 Å. While there are no indications of abnormally large errors associated with that particular hydrogen peak on the difference maps, this is a result that requires confirmation by an independent experiment. The hydrogen bond distances and angles are shown in Table 5. The non-bonded distances which are less than 3·3 Å are also listed in Table 5.

Table 4. *Conformation angles**

Within the pyranose rings

C(1) → C(2)	+56·2°	C(1′) → C(2′)	+55·7°
C(2) → C(3)	−58·4	C(2′) → C(3′)	−50·0
C(3) → C(4)	+60·5	C(3′) → C(4′)	+52·0
C(4) → C(5)	−60·1	C(4′) → C(5′)	−58·3
C(5) → O(5)	+58·3	C(5′) → O(5′)	+65·1
O(5) → C(1)	−56·2	O(5′) → C(1′)	−64·9

Outside the pyranose rings

Bond	Reference atoms	Conformation angle
C(5) → C(6)	O(5) C(5) C(6) O(6)	+60·4°
C(5′) → C(6′)	O(5) C(5) C(6′)O(6′)	−67·9
C(1′) → O(1′)	O(5′)C(1′)O(1′)C(7′)	−69·2
O(1) → C(1)	C(4′)O(1) C(1) C(2)	−128·2
	C(4′)O(1) C(1) O(5)	+110·0
O(1) → C(4′)	C(1) O(1) C(4′)C(3)	+129·2
	C(1) O(1) C(4′)C(5)	−108·9

* The conformation angle of a directed bond C(2) → C(3) is defined as the angle, measured counter-clockwise, that the projection of the bond C(1) → C(2) makes with respect to the projection of the bond C(3) → C(4). The angle is positive if it is measured clockwise (Klyne & Prelog, 1960).

The bond lengths and bond angles with their standard deviations are shown in Table 6. The C–C bond lengths range from 1·510 to 1·535 Å and none differ

Table 5. *Hydrogen bond distances and angles*

i	*j*	*k*	*D*(*ij*)	*D*(*jk*)	Angle *ijk*
C(2)	O(2)	O(3′)		2·825 Å	118·2°
C(2)	O(2)	O(3′) (*a*)		2·694	140·9
C(3)	O(3)	O(4) (*b*)		2·762	135·0
C(3)	O(3)	O(2′) (*a*)		2·877	131·1
C(4)	O(4)	O(3) (*b*)		2·762	94·4
C(4)	O(4)	O(2′) (*c*)		2·997	148·0
C(6)	O(6)	O(*W*)		2·859	113·3
C(6)	O(6)	O(*W*)(*d*)		2·769	121·4
C(2′)	O(2′)	O(3) (*e*)		2·877	150·9
C(2′)	O(2′)	O(4) (*f*)		2·997	115·5
C(3′)	O(3′)	O(2)		2·825	117·8
C(3′)	O(3′)	O(2) (*e*)		2·694	104·1
C(6′)	O(6′)	O(*W*)		2·802	103·5
C(6′)	O(6′)	O(*W*)(*g*)		2·803	104·0
O(6)	O(*W*)	O(6) (*h*)	2·859 Å	2·769	118·7
O(6′)	O(*W*)	O(6′) (*g*)	2·802	2·803	79·0
O(6)	O(*W*)	O(6′)	2·859	2·802	96·9
O(6)	O(*W*)	O(6′) (*g*)	2·859	2·803	108·1
O(6)(*h*)	O(*W*)	O(6′)	2·769	2·802	114·7
O(6)(*h*)	O(*W*)	O(6′) (*g*)	2·769	2·803	127·9
O(*W*)	O(6)	O(*W*)(*d*)	2·859	2·769	118·7
O(*W*)	O(6′)	O(*W*)(*g*)	2·802	2·803	97·7

Intermolecular non-bonded distances less than 3·3 Å.

i	*j*	*D*(*ij*)
O(3)	O(3)(*b*)	3·300 Å
O(3)	C(4)(*b*)	3·208
O(5)	O(*W*)	3·257

Table 5 (*cont.*)

Symmetry Code

—	x	y	z
a	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$-z$
b	$1-x$	y	$-z$
c	$\frac{1}{2}+x$	$-\frac{1}{2}+y$	z
d	x	$-1+y$	z
e	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$-z$
f	$-\frac{1}{2}+x$	$\frac{1}{2}+y$	z
g	$1-x$	y	$1-z$
h	x	$1+y$	z

significantly from the mean value of 1·520 Å. The C–O bond lengths, excluding the C(1′)–O(1′), range from 1·408 to 1·440 Å with the mean value of 1·427 Å. The bond length of C(1′)–O(1′) is 1·375 Å, which is shorter than the mean value by 7σ. The comparative shortening of a C(1)–O(1)H link has been observed in five other structure determinations of pyranose sugars at significant levels varying between ($\Delta = 2\sigma$) and ($\Delta = 7\sigma$), but this is the first such observation in a glucoside derivative (*cf.* Kim & Jeffrey, 1967). In contrast, the corresponding α-glycosidic link, C(1)–O(1), is 1·416 Å, which is not significantly different from the mean value. Associated with this normal C–O bond length, there is an apparent inequality of the ring C–O bonds. That adjacent to the anomeric C(1) is shorter by 0·032 Å,

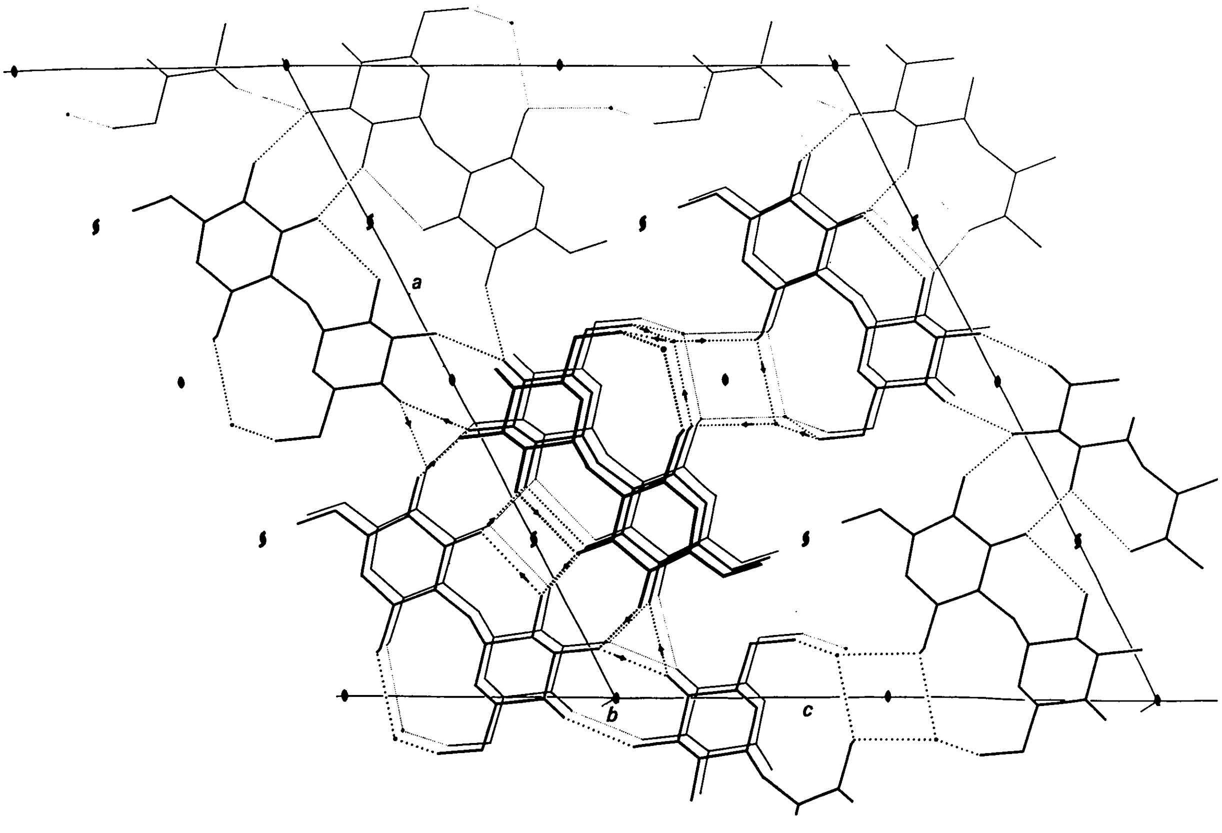

Fig. 2. The molecular packing and hydrogen bonding in methyl β-maltopyranoside monohydrate. The dotted lines are hydrogen bonds. The arrows indicate the donor-acceptor direction.

which corresponds to 3·5σ and is therefore probably significant. The acceptance of this as a characteristic feature associated with an 'unshortened' glucosidic link is strongly supported by a similar result observed in the α-glucopyranose residue of sucrose at a higher significance level (10σ) by Brown & Levy (1963). The C–O bond lengths in the three disaccharides which have been studied are summarized in Table 7. The results of this work and of that on sucrose are consistent with the data on the monosaccharides (Kim & Jeffrey, 1967), if the following 'rules' are adopted:

Table 6. *Bond lengths and bond angles* (*with estimated standard deviations in parentheses referred to the last decimal positions of respective values*)

C(1)–C(2)	1·514 (8) Å	O(5)–C(1)–O(1)	111·5 (4)°
C(2)–C(3)	1·516 (8)	C(2)–C(1)–O(1)	107·8 (5)
C(3)–C(4)	1·531 (8)	C(2)–C(1)–O(5)	110·9 (5)
C(4)–C(5)	1·533 (8)	C(1)–C(2)–O(2)	110·2 (5)
C(5)–C(6)	1·526 (9)	C(3)–C(2)–O(2)	112·4 (5)
		C(1)–C(2)–C(3)	111·1 (5)
C(1)–O(1)	1·416 (7)	C(2)–C(3)–O(3)	110·4 (5)
C(1)–O(5)	1·408 (7)	C(4)–C(3)–O(3)	108·6 (5)
C(2)–O(2)	1·428 (7)	C(2)–C(3)–C(4)	106·1 (5)
C(3)–O(3)	1·422 (8)	C(3)–C(4)–O(4)	111·1 (5)
C(4)–O(4)	1·435 (7)	C(5)–C(4)–O(4)	109·4 (5)
C(5)–O(5)	1·440 (7)	C(3)–C(4)–C(5)	109·1 (5)
C(6)–O(6)	1·428 (8)	C(4)–C(5)–O(5)	108·8 (5)
		C(6)–C(5)–O(5)	106·4 (5)
C(1′)–C(2′)	1·510 (9)	C(4)–C(5)–C(6)	111·7 (5)
C(2′)–C(3′)	1·535 (8)	C(5)–C(6)–O(6)	111·4 (5)
C(3′)–C(4′)	1·513 (8)		
C(4′)–C(5′)	1·512 (8)	O(5′)–C(1′)–O(1′)	107·1 (5)
C(5′)–C(6′)	1·513 (9)	C(2′)–C(1′)–O(1′)	108·9 (5)
		C(2′)–C(1′)–O(5′)	110·3 (5)
C(1′)–O(1′)	1·375 (8)	C(1′)–C(2′)–O(2′)	110·9 (5)
C(1′)–O(5′)	1·427 (7)	C(3′)–C(2′)–O(2′)	107·7 (5)
C(2′)–O(2′)	1·419 (8)	C(1′)–C(2′)–C(3′)	109·8 (5)
C(3′)–O(3′)	1·429 (7)	C(2′)–C(3′)–O(3′)	111·1 (5)
C(4′)–O(1)	1·438 (7)	C(4′)–C(3′)–O(3′)	107·4 (5)
C(5′)–O(5′)	1·430 (7)	C(2′)–C(3′)–C(4′)	110·7 (5)
C(6′)–O(6′)	1·437 (8)	C(3′)–C(4′)–O(1)	107·9 (4)
C(7′)–O(1′)	1·425 (11)	C(5′)–C(4′)–O(1)	111·1 (5)
		C(3′)–C(4′)–C(5′)	111·0 (5)
		C(4′)–C(5′)–O(5′)	108·2 (5)
		C(6′)–C(5′)–O(5′)	108·4 (5)
		C(4′)–C(5′)–C(6′)	115·3 (5)
		C(5′)–C(6′)–O(6′)	110·7 (5)
		C(1) –O(1) –C(4′)	117·6 (4)
		C(1) –O(5) –C(5)	114·7 (4)
		C(1′)–O(1′)–C(7′)	113·2 (6)
		C(1′)–O(5′)–C(5′)	111·5 (4)

I. An axial glycosidic bond is short only when the hydrogen atom on O(1) is unsubstituted, as suggested by Robertson & Sheldrick (1965).

II. An equatorial glycosidic C(1)–O(1) bond is short irrespective of whether the hydrogen atom on O(1) is substituted or not.

III. When there is a shortening of the C(1)–O(1) bond length, no significant differences have been observed in the ring C–O bond lengths.

IV. If the C(1)–O(1) bond is not significantly short, the two ring C–O bond lengths are possibly different, with that adjacent to the glycosidic link the shorter.

These bonds form the hemiacetal group of the pyranose ring, the properties of which give rise to much of the variety in carbohydrate chemistry in aqueous solution. It is well known to be very sensitive to intra- and inter-molecular environments, but no theoretical treatment has yet been suggested which could provide a basis for comparison with these observations.

Valence angles lie within the range commonly found in pyranose sugars (*cf.* Jeffrey & Rosenstein, 1964). The internal angles of the carbon atoms in the rings range from 106·1 to 111·1°, with the mean value of 109·4°, and those outside the ring range from 107·1 to 115·2° with the mean value of 110·0°. The valence angles of the ring oxygen atoms are 114·7 and 111·5°. The angle at the β-glycosidic oxygen is 113·2° and that joining the two glucopyranose units is 117·6°, which compares with 116·7° in cellobiose (Brown, 1966), 114·4° in sucrose (Brown & Levy, 1963) and 119·1° in cyclohexaamylose–potassium iodide (Hybl *et al.*, 1965). The configuration of the molecule, the intra- and

Table 7. *Comparison of* C–O *bond lengths in disaccharides*

	Configuration of C(1)–O(1) bond	Bond length of C(1)–O(1)	Shortening of C(1)–O(1) bond (from mean)	Bond length of ring C–O		Difference between two ring C–O bond lengths
				C(1)–O(5)	C(5)–O(5)	
Methyl β-maltoside monohydrate	axial*	1·416	1·5 σ	1·408	1·440	3·5 σ
(Chu & Jeffrey, this work)	equatorial†	1·375	7 σ	1·427	1·430	none
Cellobiose	equatorial*	1·373	7 σ	1·458	1·406	6 σ
(Brown, 1966)	equatorial‡	1·389	5 σ	1·453	1·423	3·5 σ
Cellobiose	equatorial*	1·38	2·5 σ	1·45	1·38	2·5 σ
(Jacobson *et al.*, 1961)		(1·43)§	(none)	(1·46)	(1·43)	(1·5 σ)
	equatorial‡	1·40	1·5 σ	1·35	1·47	4 σ
		(1·41)	(none)	(1·38)	(1·43)	(2·5 σ)
Sucrose residue (α-glucose) (Brown & Levy, 1963)	axial*	1·420	none	1·408	1·436	10 σ

* C–O–sugar.
† C–OCH_3.
‡ C–OH.
§ Values in parentheses are results from anisotropic refinement of these data by Sundaralingam (1965).
σ = Estimated standard deviations as quoted by authors.

intermolecular distances and bond angles were calculated with IBM 1620 programs by Chu & Shiono (1963).

The thermal ellipsoid parameters given in Table 3 and the illustration in Fig. 1 (Johnson, 1965) show that the molecule as a whole has no marked thermal anisotropy. As in the structure of cellobiose (Brown, 1966), all the oxygen atoms appear to have higher vibration amplitudes perpendicular to their C–O bonds than along them. The methyl group has a high thermal motion consistent with its van der Waals environment around the twofold axes (see Fig. 2).

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Crystal Structure of Ethyl-1-thio-α-D-glucofuranoside

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The crystal structure of ethyl-1-thio-α-D-glucofuranoside ($C_8H_{16}O_5S$) has been determined by three-dimensional Patterson and Fourier syntheses. The structure was refined by block-diagonal least squares. The final *R* value for the structure with the correct absolute configuration was 8·9% for the 1030 observed reflections. The absolute configuration of the molecule was determined from the anomalous scattering of Cu *Kα* radiation by the sulfur atom. The geometry of the molecules is, in general, in accord with previous studies on monosaccharides. The conformation of the furanose ring seems to be slightly different from that observed in other compounds. The stacking of the molecules and the hydrogen bonding scheme are illustrated.

Introduction

The furanose ring occurs in a variety of important biological molecules, particularly in the nucleic acids and other carbohydrate derivatives. Information on the conformations of the furanose moieties is of considerable importance in nucleic acid model building. The present study on ethyl-1-thio-α-D-glucofuranoside was undertaken in order to supply additional precise information about the stereochemistry of furanoid rings.

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